The free energy of carbon monoxide can be expressed by the equation

$$\Delta F = -26{,}080 - 20.9T \quad (28)$$

Combining this with (22) and (23), we have for the synthesis of methanol and other alcohols, respectively, from carbon monoxide and hydrogen

$$\Delta F = -26{,}370 + 49.9T \quad (29)$$
$$\Delta F = -17{,}460 - 7010n + 20.9T + 24.2nT \quad (30)$$

Applying (29), we have for the methanol synthesis

° C.	ΔF	$K = \frac{(CH_3OH)}{(CO)(H_2)^2}$
227	−1420	4.17
327	+3570	0.05
427	+8560	0.0021

Synthesis of Methanol from Carbon Monoxide and Hydrogen[1]

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A study has been made of some of the factors governing the synthesis of methanol from carbon monoxide and hydrogen under high pressure and in the presence of a catalyst. The literature on methanol catalysts is discussed in the light of experimental data, and the methanol equilibrium as calculated from thermal data is compared with results obtained with a catalyst composed of the oxides of copper, zinc, and aluminum.

The methanol formed by the reaction has a purity of between 99 and 100 per cent provided that the variables temperature, pressure, and rate of flow are chosen within the limits most desirable from the point of view of maximum yield. Under these same conditions only a small amount of carbon monoxide is lost in wasteful side reactions, leading to the formation of carbon dioxide, methane, and water. Studies made with several chambers in series have demonstrated that the catalyst contained in the first chamber protects the catalyst in successive chambers against poisoning.

IN THE spring of 1925, when the experimental work on the high-pressure synthesis of methanol from carbon monoxide and hydrogen was initiated in this laboratory, considerable publicity had already been given to the new methanol synthesis, although actual data on operation of the process were meager. A German patent of 1913[2] covered the process of synthesizing oxygenated organic compounds from carbon monoxide and hydrogen in a broad and general way, while more specific information was available in a patent and a paper by Patart.[3] An article by Audibert also appeared at that time.[4] From these sources it was apparent that methanol could be produced by passing a mixture of carbon monoxide and hydrogen over a heated metallic oxide catalyst at high pressure.

Thermodynamic Considerations

The simplest possible reactions involving carbon monoxide and hydrogen are as follows:

$$CO + H_2 = HCHO + 2000 \text{ cal.} \quad (1)$$
1 vol. 1 vol. 1 vol.

$$CO + 2H_2 = CH_3OH + 24{,}685 \text{ cal.} \quad (2)$$
1 vol. 2 vols. 1 vol.

$$CO + 3H_2 = CH_4 + H_2O + 50{,}000 \text{ cal.} \quad (3)$$
1 vol. 3 vols. 1 vol. 1 vol.

$$2CO + 2H_2 = CH_4 + CO_2 + 60{,}282 \text{ cal.} \quad (4)$$
2 vols. 2 vols. 1 vol. 1 vol.

(The heats of reaction are for reactants and products in the gaseous state.)

The third and fourth of these, the methane reactions, have been studied in detail by Sabatier and his associates,[5] and data on the equilibria are available through the researches of Mayer and co-workers.[6] Apparently methane was the only organic product derived from the reduction of carbon monoxide with hydrogen at atmospheric pressure, as evidenced by Sabatier's extensive investigations,[5] although a number of patents claim the possibility of securing small yields of formaldehyde and even methanol.[7]

From a consideration of the volumes entering in the reactions it is apparent that the formation of methanol goes with the largest volume decrease—viz., from three to one and hence would be most favored by increased pressure. The parallelism between the methanol reaction and the reaction for synthesis of ammonia is striking in this respect.

Calculations of the methanol equilibrium are bound to be more or less inaccurate owing to the lack of adequate data on the specific heat and the equation of state of the alcohol. The fact that the synthesis is carried out at temperatures of 300° C. and up—that is, in the neighborhood of and above the critical temperature of methanol (240° C.)—further reduces the quantitative significance of equilibrium calculations. In a qualitative way, however, free-energy considerations show how the tendency for the reaction to go varies with temperature. Calculations of the free energy of the reaction are now available in the literature and check within the limits of error with those made in this laboratory at the start of the present investigation:

For the reaction, $CO_{(gas)} + 2H_{2(gas)} = CH_3OH_{(gas)}$

$$\Delta F = -20{,}480 + 43.1\,T \log T - 0.01545\,T^2 - 69.8\,T$$

$\Delta F_{300°\text{ A.}}$	$\Delta F_{700°\text{ A.}}$	Authors
−10,810	+8930	
−10,800	+9050	Kelley[8]
−10,790	+9242	Smith[9]

[1] Received January 18, 1928.

[2] German Patent 293,787 (March 8, 1913), with additions 295,202 (May 31, 1914) and 295,203 (June 23, 1914); French Patent 468,427 (February 13, 1914); British Patent 20,488 (1915); U. S. Patent 1,201,850 (October 17, 1916).

[3] French Patent 540,343 (August 19, 1921); *Chimie & industrie*, **13**, 179 (1925); *Compt. rend.*, **179**, 1330 (1924); see also Lormand, *Ind. Eng. Chem.*, **17**, 430 (1925).

[4] *Chimie & industrie*, **13**, 186 (1925),

[5] *Compt. rend.*, **124**, 1358 (1897); *Ann.*, **3447**, 34, 360, 418, 435, 477 (1905); *Ann. chim. phys.*, [8] **4**, 418 (1905).

[6] *J. Gasbel.*, **52**, 166, 194, 242, 326 (1909). A complete review of the literature on the subject up to 1923 is contained in a paper by Haslam and Forrest, *Gas Age-Record*, **52**, 615 (1923).

[7] Jahn, *Ber.*, **32**, 989 (1899); Orlow, *Chem. Zentr.*, **801**, 735 (1909); Dreyfus, British Patents 108,855 (July 23, 1917); 157,047 (August 25, 1917); Calvert (editorial), *Chem. Age (London)*, **5**, 153 (1921); Bone and Wheeler, *J. Chem. Soc. (London)*, **81**, 541 (1902); **83**, 1074 (1903). Likewise, the following references have direct bearing on the subject: Berthelot, *Ann. chim. phys.*, [5] **10**, 72 (1877); Losanitch and Jovitschich, *Ber.*, **30**, 135 (1897); Hemptine, *Chem. Zentr.*, **76**, 171 (1905); Berthelot and Gaudechon, *Compt. rend.*, **150**, 1690 (1910).

[8] *Ind. Eng. Chem.*, **18**, 78 (1926).

[9] *Ibid.*, **19**, 801 (1927).

It is interesting to note that the equilibrium constant of the reaction changes with temperature in such a manner that at atmospheric pressure and room temperature methanol would be perfectly stable, while at 300° C. equilibrium would be attained with less than 2 per cent methanol, starting with a mixture of carbon monoxide and hydrogen in the theoretical ratio of 1:2. Even with the best catalysts it has apparently been impossible to suppress the reaction temperature much below 300° C., corresponding practically to no methanol at atmospheric pressure. This clearly shows why past attempts to synthesize methanol from the gases in question at atmospheric pressure were bound to meet with failure. On the other hand, the calculations indicate that at a pressure of 1000 pounds per square inch, or 68

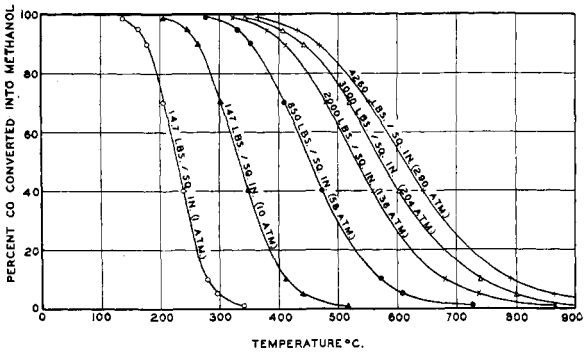

Figure 1—Theoretical Conversion of Carbon Monoxide into Methanol as a Function of Temperature at Various Pressures, Calculated from Thermal Data for a Gas Mixture Consisting of 26% CO, 70% H_2, and 4% Inert

Reaction: $CO + 2H_2 \rightleftarrows CH_3OH + 24{,}685$ cal.

atmospheres, the equilibrium would still be favorable to practically 100 per cent methanol at 300° C. Even with selective catalysts it becomes desirable, however, to employ considerably higher pressure in order to favor methanol formation at the expense of the two methane reactions. Furthermore, it is to be expected that the rate of reaction increases with pressure owing to the higher concentrations.

Figures 1 and 2 give the calculated percentages of carbon monoxide converted to methanol at equilibrium for any combination of temperature and pressure. The calculations are for a gas mixture containing 26 per cent carbon monoxide and 70 per cent hydrogen in order to permit direct comparison with the experimental results reported later in this paper.

Types of Catalysts Used in Synthesis of Methanol

In addition to the papers and patents cited above, there has appeared during the last two years a great deal of information relative to the types of catalysts suitable for methanol formation.[10] The most important group of catalysts consists of combinations of non-reducible metallic oxides in which it is generally essential to have the most basic component present in preponderating quantities.[11] While a number of the first patents claimed the necessity of complete exclusion of iron from the reaction zone, it is now generally agreed that iron may be present, presumably in a non-active form.[12]

[10] U. S. Patents 1,558,559 (October 27, 1925); 1,569,775 (September 4, 1924); German Patent 415,686 (July 24, 1923); French Patents 571,285 (May 14, 1924); 571,354 (May 16, 1924); 571,355 (May 16, 1926); 571,356 (May 16, 1924); 575,913 (August 8, 1924); 581,816 (December 6, 1924); 581,169 (February 23, 1925); British Patents 227,147 (1925); 228,959 (1925); 229,714 (1925); 229,715 (1925); 231,285 (1925); 237,030 (1925); 238,319 (1925); 240,955 (1925); 254,760 (1926); French Patent 540,543 (July 12, 1922); *Tech. Eng. News*, December, 1926.

[11] U. S. Patent 1,558,559 (October 27, 1925); French Patent 571,354 (May 16, 1924); British Patent 227,147 (1925).

[12] British Patent 254,760 (1926); U. S. Patents 1,608,643 (November 30, 1926); 1,609,593 (December 7, 1926); 1,625,924; 1,625,925; 1,625,926; 1,625,927; 1,625,928; 1,625,929 (April 26, 1927).

The term "non-reducible," when referring to the oxides used as catalysts, becomes rather indefinite. A compound like zinc oxide, for example, which normally is not reduced by carbon monoxide or hydrogen at the temperatures in question (300° to 400° C.) shows all indications of being at least partially reduced, when intimately mixed with copper oxide.[13] It has even been stated[14] that metallic oxides which, when alone, are reduced to the corresponding metals do not completely part with their oxygen when mixed with more basic oxides.

Patart[3] claims to have based his catalyst search in connection with the methanol synthesis, on the observations by Sabatier and Maihle[15] and Jahn[16] on the reverse reaction—i. e., the catalytic decomposition of methanol at elevated temperatures. After having tried a number of the individual catalysts studied by these investigators, Patart, however, ultimately came to the conclusion that mixed catalysts were required for best results, although the data disclosed in his first paper would indicate that zinc oxide alone is a good catalyst. Similar observations on zinc oxide are reported by Fischer,[17] but the present writers have not had much success with catalysts consisting of a single oxide. In general, it has been found advantageous to use mixtures of two or more metallic oxides of which one, at least, is non-reducible with reference to carbon monoxide and hydrogen under atmospheric pressure at the temperature in question.

Owing to the exothermic character of the methanol reaction, 26,150 calories per mol of gaseous methanol formed at 327° C., it was found beneficial to support the catalyst on a good heat conductor in order to prevent local overheating of the contact material. Granulated metallic copper proved satisfactory for this purpose.

While a large number of catalysts have been studied, the data reported below were all obtained with a mixture originally consisting of 36 per cent zinc oxide, 44 per cent copper oxide, and 20 per cent aluminum oxide supported on metallic copper, the ratio of active catalyst to copper support being 1:3. This catalyst is of medium activity.

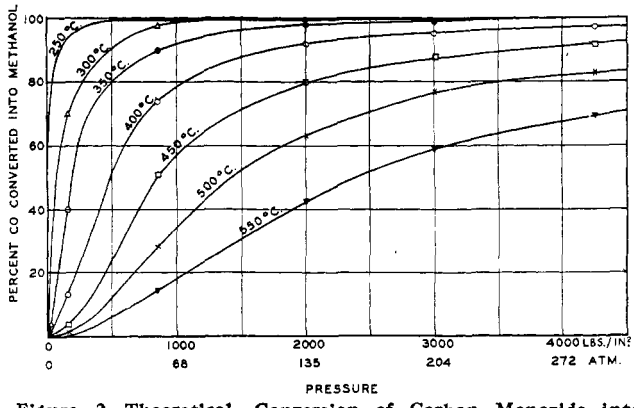

Figure 2—Theoretical Conversion of Carbon Monoxide into Methanol as a Function of Pressure at Various Temperatures, Calculated from Thermal Data for a Gas Mixture Consisting of 26% CO, 70% H_2, and 4% Inert

Reaction: $CO + 2H_2 \rightleftarrows CH_3OH + 24{,}685$ cal.

Method of Preparing Catalyst

A study of different ways of preparing catalysts for methanol synthesis led to the adoption of a method similar to

[13] This observation is supported by a statement in British Patent 237,030 (1925) and by a paper by Rogers, *J. Am. Chem. Soc.*, **49**, 1432 (1927).

[14] British Patent 254,760 (1926).

[15] *Compt. rend.*, **146**, 1376 (1908); **148**, 1734 (1909); "Catalysis in Organic Chemistry," p. 678 (1923).

[16] *Ber.*, **12**, 983 (1880).

[17] "Conversion of Coal into Oils," 1925; *Ind. Eng. Chem.*, **17**, 574 (1925).

the one described by Evans and Newton.[18] The hydroxides of the metals in question are precipitated by ammonium hydroxide from an aqueous solution of the nitrates at 85° C., the purest grade of chemicals being used throughout. Upon careful washing, the hydroxides are obtained as a gel into which the supporting copper is mixed prior to drying at 110° C. A granular, rugged catalyst may thus be obtained.

After having been placed in the reactor, the catalyst is brought up to a temperature of 180° to 200° C. and subjected to the action of the carbon monoxide-hydrogen mixture under reduced pressure, say 100 to 400 pounds per square inch (6.8 to 26.1 atmospheres), for 2 to 4 hours. During this process the copper oxide is presumably reduced to metallic copper, while the hydrated aluminum oxide is dehydrated partly, but probably not completely. Reduction to lower stages of oxidation of the zinc and aluminum may also take place, since this has been shown to be the case for zinc oxide mixed with copper oxide, as mentioned above.

Apparatus

A diagrammatic layout of the apparatus used for the synthesis of methanol is shown in Figure 3. The essential features are (1) mixing of the carbon monoxide and hydrogen in desired proportions, (2) compression of the gas mixture, (3) oil filtration, (4) further purification of gases if desired, (5) storage of compressed gas to provide for intermittent compression, (6) regulation of pressure of outflowing gas by means of proper reducing valves, (7) reaction of carbon monoxide and hydrogen in electrically heated chrome vanadium steel reactors, (8) condensation under pressure of the liquid product in water-cooled condensers, (9) separation of liquid from gas, followed by (10) discharge of liquid and gas through separate valves and (11) determination of liquid yield and of exit gas flow. Valves are installed for withdrawal of gas samples for analysis and special holders are connected with the exit gas lines to permit collection of composite samples. The diagram also shows alternative connections for operation of two or three chambers in series. High-pressure flowmeters may be inserted at the entrance to the reactors, although the entering gas flow can readily be followed from the exit rate when correction is made for the products formed per unit time.

The reaction chambers are constructed of chrome-vanadium steel with bolted-on heads. They are copper-lined and provided with thermocouple wells permitting measurement of the temperature of the gas in the reaction zone or at any other point throughout the reactor. The catalyst occupies only about one-third of the free space in the chamber, the lower and upper parts being filled with copper shot to secure good temperature control.

[18] *Ind. Eng. Chem.*, **18**, 513 (1926).

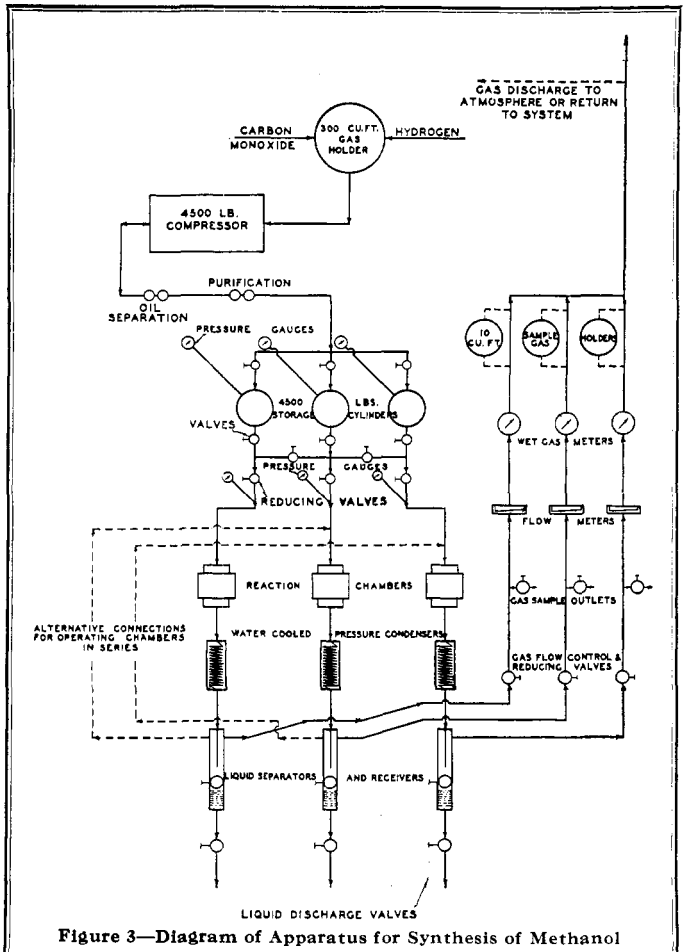

Figure 3—Diagram of Apparatus for Synthesis of Methanol

Effect of Different Variables on Operation of Methanol Process

With a mixture of carbon monoxide and hydrogen flowing through the reactor at pressures from about 1000 pounds per square inch (68 atmospheres) and up, methanol begins to form as soon as the temperature of the catalyst has reached about 300° C. The minimum reaction temperature varies with the catalyst and decreases somewhat with increasing pressure, but rarely goes below 280° C.

While the thermodynamic calculations presented graphically in Figures 1 and 2 predict the temperature and pressure ranges within which the process may be operated most successfully, they fail to take into account two essential variables: (1) rate of reaction, or space-time yield, and the effect of temperature on it; and (2) change in activity of the catalyst with time and temperature, as well as its susceptibility to poisoning. Hence it becomes necessary to study the effect of these different factors by actual experiments.

Figure 4 gives the rate of methanol formation as a function of the rate of entering gas flow under a constant pressure of 3000 pounds per square inch (204 atmospheres). It appears that the yield of methanol is a linear function of the rate of gas flow. No attempt will be made to explain this result at present, since the effect of rate of diffusion and other factors involved are not known.

From Figure 4 it will also be noticed that the methanol yield decreases with increasing temperature. No data are given on this plot for 300° C., because it was impossible to get a representative curve from the observations made at that temperature in this series of experiments. The irregular results at 300° C. are not surprising when it is considered that this is, practically speaking, the temperature at which the reaction starts, and it is well known that results are hard to reproduce at the point where a catalyst commences to become active, especially when the reaction in question is exothermic.

While the quantity of methanol formed per unit time increases with the rate of gas flow, the percentage conversion of carbon monoxide decreases owing to the shorter time of contact between the reacting gas and the catalyst. Percentage conversion *vs.* rate of flow is plotted in Figure 5 for various temperatures at 3000 pounds pressure (204 atmospheres). The curve for 300° C. is somewhat uncertain on account of the wide variations in the ob-

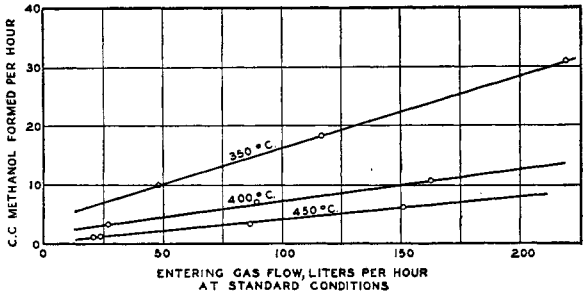

Figure 4—Yield of Methanol as a Function of Rate of Gas Flow

Using 40 cc. of catalyst at various temperatures at a pressure of 3000 lbs. per sq. in. (204 atmos.). Ratio CO: H_2 in entering gas about 0.37

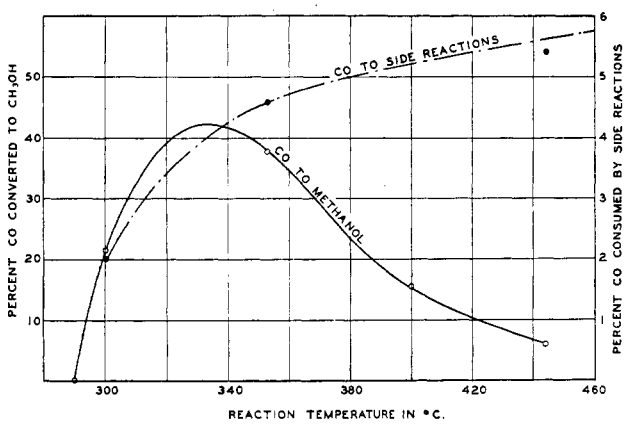
PERCENT CO CONVERTED TO CH3OH
PERCENT CO CONSUMED BY SIDE REACTIONS
CO TO SIDE REACTIONS
CO TO METHANOL
REACTION TEMPERATURE IN °C.

Figure 6—Effect of Temperature on Methanol Reaction

Entering gas rate 80 liters per hour at standard conditions using 40 cc. of catalyst at a pressure of 3000 lbs. per sq. in. (204 atmos.). Ratio CO: H_2 in entering gas about 0.37

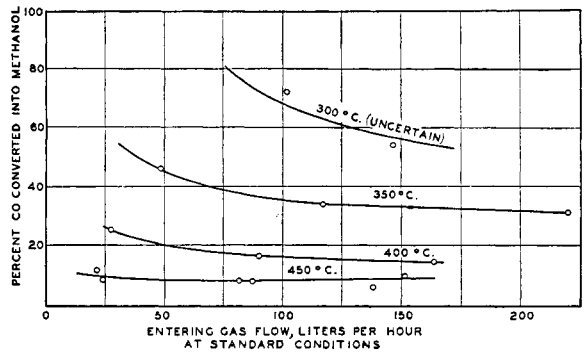

Figure 5—Conversion of Carbon Monoxide into Methanol as a Function of Rate of Gas Flow

Using 40 cc. of catalyst at various temperatures at a pressure of 3000 lbs. per sq. in. (204 atmos.). Ratio CO: H_2 in entering gas about 0.37

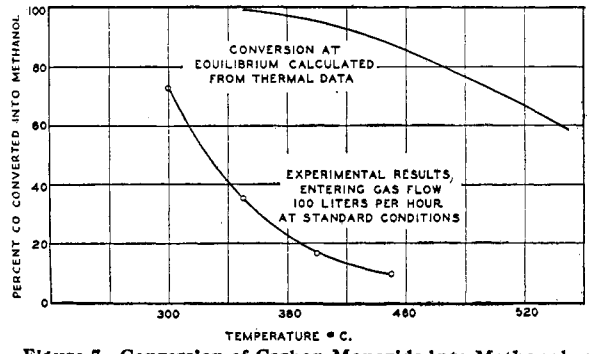
PERCENT CO CONVERTED INTO METHANOL
CONVERSION AT EQUILIBRIUM CALCULATED FROM THERMAL DATA
EXPERIMENTAL RESULTS, ENTERING GAS FLOW 100 LITERS PER HOUR AT STANDARD CONDITIONS
TEMPERATURE ° C.

Figure 7—Conversion of Carbon Monoxide into Methanol as a Function of Temperature at a Pressure of 3000 lbs. per sq. in. (204 atmos.)

Experimental curve obtained by using 40 cc. of catalyst with a gas mixture having a ratio of CO: H_2 of about 0.37

servations, the highest yields obtained at this temperature being used in plotting the curve.

The yield of methanol under otherwise constant conditions passes through a maximum as the temperature is raised. Figure 6 shows this graphically for another series of experiments than that plotted in Figure 5. Again the conversion at 300° C. is uncertain, but regardless of the exact location of this point, the fact remains that the reaction starts at 290° C., increases very rapidly with the temperature, passes through a maximum somewhere between 300° and 350° C., and then falls off considerably as the temperature is increased to 450° C.

Figure 7 shows the percentage conversion of carbon monoxide to methanol as a function of temperature at 3000 pounds pressure (204 atmospheres) and an entering gas flow of 100 liters per hour. The upper curve represents the theoretical conversion at equilibrium as calculated from thermal data. The plot does not permit any conclusions as to the validity of the thermodynamic calculations, since these calculations are based on equilibrium conditions, while the experimental results are obtained at a rate of flow at which we know for a certainty that equilibrium is not attained. The interesting point about these curves is that they bring out the decrease in the activity of the catalyst with increasing temperature. Even though the calculated curve may not be exactly correct owing to the uncertainty attached to the calculations, its course is characteristic of this type of reactions. Hence, the experimental curve should have displayed a somewhat similar slope had the activity of the catalyst stayed constant. This particular way of plotting the results, therefore, permits a study of the change in activity with rising temperature. That the activity actually had decreased was demonstrated by the fact that a catalyst, once operated at a higher temperature, had suffered a permanent change as evidenced by its reduced activity when again run at lower temperature. It is possible that this temperature effect may be due to a progressive dehydration of the partly hydrated aluminum oxide contained in this particular catalyst.

The effect of pressure upon the conversion at constant temperature (300° C.) and constant rate of flow (150 liters per hour of entering gas) is shown in Figure 8. The calculated curve is included for comparison. The calculated data are for complete equilibrium while the experimental results are not. It will be seen that the percentage conversion as determined by experiment increases considerably with pressure in a range where the calculated conversion changes only from 98 to 99.5 per cent. The increased methanol formation is obviously in part due to the longer time of contact, inasmuch as the plot is based on constant rate of entering gas flow and therefore does not take into account that the actual rate in the chamber is lowered with increasing pressure.

Character of Methanol Formed

The alcohol produced by reaction of carbon monoxide and hydrogen at, say, 3000 pounds pressure (204 atmospheres) and at not too high a temperature is very pure, as evidenced by a specific gravity corresponding to 99–100 per cent methanol. The odor is that of pure methanol, and combustion analysis gives a ratio of carbon to hydrogen and oxygen corresponding to the formula CH_3OH.

Side Reactions

From the analysis of the liquid product it is evident that side reactions do not occur to any appreciable extent under

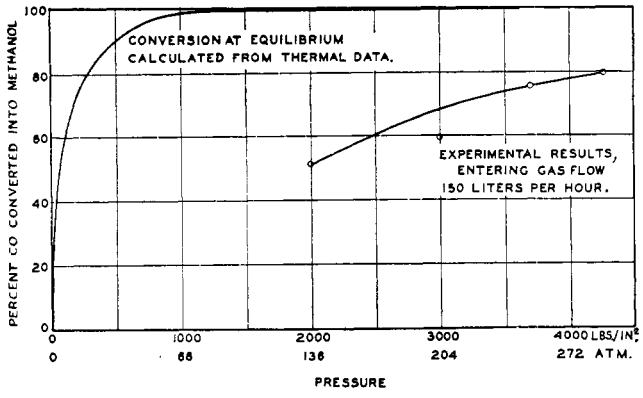

Figure 8—Conversion of Carbon Monoxide into Methanol as a Function of Pressure at 300° C.

Experimental curve obtained by using 40 cc. of catalyst with a gas mixture having a ratio of CO : H_2 of about 0.37

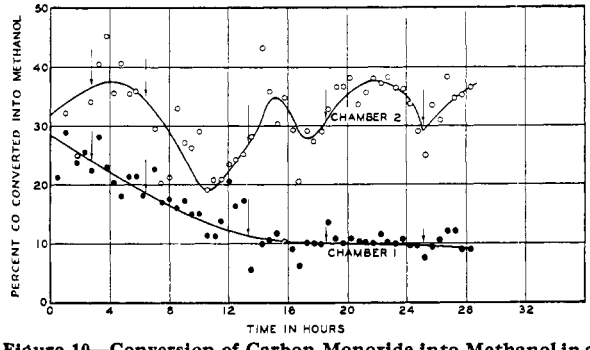

Figure 10—Conversion of Carbon Monoxide into Methanol in a Discontinuous Run with Two Chambers in Series

Gas entering chamber 1 has a ratio of CO : H_2 = 0.322; chamber 1 contains 20 cc. catalyst, chamber 2, 40 cc.; pressure 3000 lbs. per sq. in. (204 atmos.), temperature 300° C.; gas leaves chamber 2 at a rate of 80 liters per hour at standard conditions; arrows indicate interruption of experiment

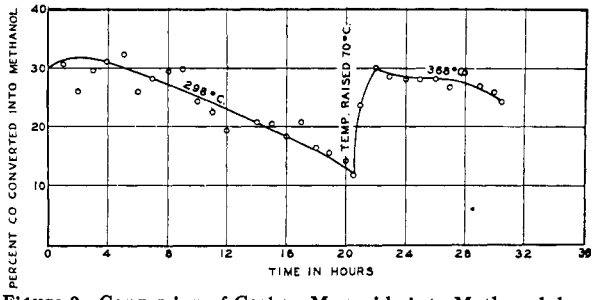

Figure 9—Conversion of Carbon Monoxide into Methanol during a Continuous Run

Ratio of CO : H_2 in entering gas = 0.458. Pressure 3000 lbs. per sq. in. (204 atmos.); temperature 298° and 368° C.; exit gas rate 80 liters per hour at standard conditions

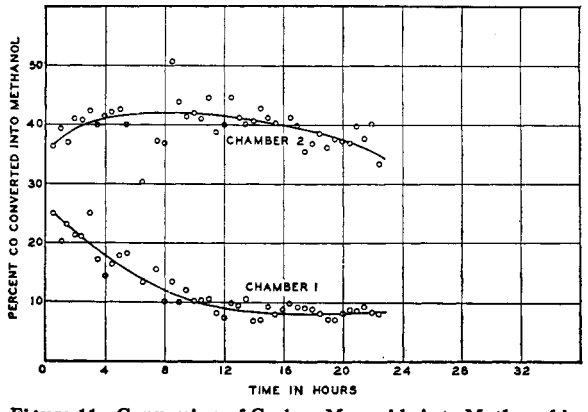

Figure 11—Conversion of Carbon Monoxide into Methanol in a Continuous Run with Two Chambers in Series

Gas entering chamber 1 has a ratio of CO : H_2 = 0.473; chamber 1 contains 20 cc. catalyst, chamber 2, 40 cc.; pressure 3000 lbs. per sq. in. (204 atmos.), temperature 300° C.; gas leaves chamber 2 at a rate of 80 liters per hour at standard conditions

the most favorable conditions. If the pressure is lowered for constant temperature, however, carbon dioxide and methane begin to form, presumably according to reactions (3) and (4). Since the volume changes for both of the methane reactions are 2 to 1 while that of the methanol reaction is 3 to 1, it is apparent that a decrease in pressure will favor the methane reactions, which evolve about twice the heat of the methanol reaction. The ratio of methane to carbon dioxide in the exit gas, as well as the low water content of the methanol produced, proves that of the two reactions number (4) predominates.

Increasing the temperature at constant pressure has a similar effect as far as the side reactions are concerned, although the result is more complicated in that higher alcohols tend to form, as will be discussed in the next paper of this series. Figure 6 shows how the percentage of carbon monoxide entering into side reactions increases with increasing temperature for constant pressure. In this particular case the percentage carbon monoxide going to side reactions between 300° and 350° C., from 2 to 4 per cent, is higher than usual.

Catalyst Life and Catalyst Poisoning

In order to study the length of catalyst life, a series of experiments was run in which no attempt was made to purify the gas mixture, consisting of electrolytic hydrogen and of carbon monoxide from the decomposition of formic acid with sulfuric acid. The catalyst was the one already mentioned, prepared from the oxides of copper, zinc, and aluminum and supported on granulated copper. The percentage carbon monoxide in the entering gas varied between 23 and 31, as shown by the ratios of carbon monoxide to hydrogen given in Figures 9 to 11. The rate of flow is in this case expressed in liters per hour of exit gas at standard conditions of temperature and pressure (0° C. and 760 mm.).

In Figure 9 the percentage conversion of carbon monoxide into methanol is plotted versus time for a run which was made with a single chamber and lasted for nearly 31 hours. During the first 20 hours at an average temperature of 298° C., the yield drops from 32 to 12 per cent, showing that the activity of the catalyst decreases with the time when only a single chamber is used. Raising the temperature from 298° to 368° C. brings the yield back to 30 per cent followed by a gradual decrease as before.

The data plotted in Figures 10 and 11 were obtained with two chambers connected in series, the unconverted gas from chamber 1 being fed into chamber 2. Figure 10 represents a 24-hour discontinuous run, and Figure 11 a 23-hour continuous run. The results demonstrate that the decrease in activity is due to poisoning. Figure 11 brings this out most clearly. The conversion in the first chamber decreases from 25 per cent and reaches a constant value of about 8 per cent, while the second chamber, which is protected against poisoning by the first chamber, gives a constant yield of from 40 to 42 per cent for about 18 hours. At the end of the run the catalyst in chamber 2 commences to show a decrease in activity, which may be explained as follows: The constant state arrived at in the first chamber indicates that the catalyst contained therein has become saturated with the substances responsible for the poisoning, and these substances can therefore pass over into the second chamber. That an equilibrium actually is set up between poison con-

tained in gas and on catalyst has been shown by the Fixed Nitrogen Laboratory for another type of catalyst.[18]

The results for the discontinuous runs plotted in Figure 10 are more complicated. The interruptions (indicated by arrows) cause the activity of the catalyst in the second chamber to vary quite irregularly. It is believed that the periodic heating and cooling are responsible for the effect, although it may also be possible that the alternating relief in pressure causes the catalyst poison accumulated in the first chamber to be transferred over to the second chamber. The curve for the first chamber is essentially a duplicate of the continuous run in Figure 11.

The curves for the second chamber in a series show that the maximum activity of the catalyst is not reached until a couple of hours after the experiment is started.

While not answering the question as to the nature of the poison, these experiments bring out the important point that the first chamber in a series acts as purifier for the gas mixture in removing substances which act as catalyst poisons. Use is being made of this in the synthetic-ammonia process, and the indications are that the same method of purification is employed in the synthesis of methanol.[2]

Note—The carbon monoxide used in these experiments was made by decomposition of formic acid by sulfuric acid and hence contained sulfur compounds. Furthermore, electrolytic hydrogen from the manufacturer whose product was used in these experiments has since been found to be contaminated occasionally with illuminating gas.

Other experiments have shown that by carefully purifying the compressed gas prior to its entrance into the first chamber it is possible to cut down the degree of poisoning to such an extent that chamber number 1 simply acts as a "safety valve" for the remainder of the system. Once the poisoning effect has been eliminated, the life of the catalyst should be considerable, although there are indications that the particular contact substance dealt with here may suffer a gradual decrease in activity due to progressive dehydration of the partly hydrated aluminum oxide.

From these data on poisoning it is apparent that due care must be exercised in studying the effect of variables, like pressure and temperature, upon the methanol reaction. Hence, all the previous conclusions are based on results obtained with the second or third chamber in a series, and only after it had been demonstrated, by varying the conditions back and forth, that the results could be duplicated.

Conclusions

Methanol of high purity may readily be prepared by passing a mixture of carbon monoxide and hydrogen, preferably at a pressure of several hundred atmospheres and at temperatures between 300° and 350° C., over a catalyst composed of metallic oxides. Working with a catalyst of medium activity prepared from the oxides of copper, zinc, and aluminum, it is possible to reach nearly theoretical conversion depending upon the pressure, temperature, and rate of gas flow employed. Carbon dioxide, water, and methane may form, but the amount of carbon monoxide consumed in these side reactions is small under the conditions most favorable to methanol formation. The catalyst in question, consisting of the oxides of copper, zinc, and aluminum supported on metallic copper, appears to be most active at lower temperature and suffers a permanent decrease in activity when exposed to higher temperatures. Also the catalyst is sensitive to poisons. By connecting several chambers in series, however, it is possible to dispose of the catalyst poison in the first chamber, thus protecting the contact material contained in subsequent reactors.

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A Modified Thermoregulator[1]

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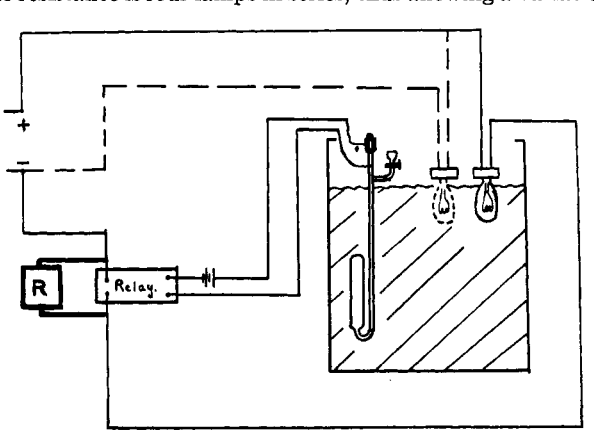
THE heating element of a thermostat is usually in two parts: (1) a constant heater which delivers heat almost but not quite sufficient to keep the bath at the desired temperature; and (2) an intermittent heater of low heat capacity, to bring the temperature up to the desired value and then to be cut off as a heat supply. This is usually accomplished by the use of two separate heaters. In small thermostats a large fraction of the total space is taken by the stirrer, regulator, and heaters. By combining the two heaters considerable space can be saved.

The accompanying figure shows the wiring diagram of the usual thermostat bath. The heavy lines show the addition necessary to make it work on a single heater. The dotted lines show the part that can be discarded. When contact is made in the mercury-toluene regulator and the relay circuit broken, the current, instead of being cut off, passes through the resistance, *R*, and the heater. When contact is broken in the mercury-toluene regulator, the current passes through the relay to the heater. The resistance, *R*, should be capable of being varied, and kept at such a value that the heat supplied by the heater when in series with the resistance is just insufficient to maintain the bath at the desired temperature.

[1] Received December 20, 1927.

The writer built a small water thermostat of this type, using as a heater a 100-watt lamp on a 230-volt d. c. circuit. The resistance is four lamps in series, thus allowing a variation



in the resistance by use of lamps of different power consumption. He found no trouble in maintaining 25°, 27.5°, and 30° ± 0.02° C.